

Amendments to the Specification:

At page 1, please replace the paragraph at lines 8-13 with the following:

This application takes priority under 35 U.S.C. 119(e) from U.S. provisional application serial number 60/502,158, filed Sept. 10, 2003. This application is a continuation-in-part of ~~pending~~ U.S. patent application Serial No. 10/382,354, filed March 5, 2003, which in turn takes priority from U.S. provisional application 60/362,167, filed March 5, 2002. Each of these applications is incorporated by reference herein to the extent that it is not inconsistent with the disclosure herein.

At page 1, please replace the paragraph at lines 16-18 with the following:

This invention was made with United States government funding ~~thought~~ through the Department of Energy National Energy Technology Laboratory Contract No. DE-FC26-00NT40762. The United States government has certain rights in this invention.

At page 2, please replace the paragraph at lines 9-14 with the following:

U.S. ~~patent~~ Patent 2,824,620 (de Rossett) relates to hydrogen-permeable membranes formed from a layer or film of hydrogen-permeable membrane on certain porous support matrices. In related U.S. ~~patent~~ Patent 2,958,391 (de Rosset) the hydrogen-permeable membrane is formed using a support matrix of sintered metal particles. U.S. Patent 3,350,846 (Makrides, et al.) reports hydrogen-permeable membranes formed from Group VB metal foils coated on both sides with palladium catalysts.

At page 2, please replace the paragraph at lines 15-21 with the following:

U.S. Patent 4,536,196 (Harris) relates to a hydrogen diffusion membrane which is palladium or a palladium alloy coated with at least one metal selected from Group IB, IVB, VB and VIB of the Periodic Table. The coating is reported to increase resistance of the palladium or palladium alloy to poisoning. U.S. ~~patent~~ Patent 4,313,013 (Harris) relates to a hydrogen diffusion membrane of palladium or certain palladium alloys that has been treated with silane and/or silicon tetrafluoride. The treatment is reported to

deposit a film of elemental silicon to prevent poisoning of the metal or alloy and extend its use before regeneration is required.

At page 3, please replace the paragraph at lines 3-14 with the following:  
U.S Patent 4,589,891 (Iniotakis et al.) reports hydrogen-permeable membranes formed by galvanic deposition of metals with high hydrogen permeability onto fine mesh metal fabric. High permeability metals are said to include Nb, Ta, V, Pd and Zr. Palladium and its alloys are said to be preferred because they are resistant to the formation of hydrides and to surface oxidation. A thin metal layer, 1 to 20 microns thick, particularly of palladium and palladium silver alloys is formed on fine metal wire mesh. The metal of the wire mesh is not specified. The patent also reports membranes formed by thin layers of hydrogen-permeable metal sandwiched between two fine metal mesh screens which provide mechanical support. The authors reported that fine metal mesh ~~were~~ was superior to porous metals as mechanical supports for thin films of palladium and palladium alloys. Related U.S. ~~patent~~ Patent 4,699,637 (Iniotakis et al.) reports hydrogen-permeable membranes formed by sandwiching a layer or foil of a hydrogen-permeable metal between two fine metal meshes to provide mechanical support.

At page 4, please replace the paragraph at lines 15-25 with the following:  
U.S. Patents 5,139,541; 5,217,506; 5,259,870; 5,393,325; and 5,498,278 (all of Edlund) relate to non-porous hydrogen-permeable composite metal membranes containing an intermetallic diffusion barrier separating a hydrogen-permeable base metal and a hydrogen-permeable coating metal. In U.S. ~~patents~~ Patents 5,139,541 and 5,217,506 the intermetallic diffusion barrier is described as a thermally stable inorganic proton conductor. A proton conductor is defined therein as any material that shows complex ion motion at high temperatures and is exemplified by the oxides and sulfides of molybdenum, silicon, tungsten and vanadium. In U.S. Patent 5,217,506, specific uses for the hydrogen transport membranes which include decomposition of hydrogen sulfide and extraction of hydrogen from a water-gas shift mixture of gases are discussed. U.S. Patent 5,259,870 reports the use of oxides of aluminum, lanthanum and yttrium as the diffusion barriers.

At page 5, please replace the paragraph at lines 15-18 with the following:

U.S. patent Patent 6,475,268 (Thornton) reports a supported membrane for hydrogen separation in a fuel cell in which the membrane is formed by deposition of a metal alloy over a foil substrate that is microetched. Exemplified metal alloys are Pd/Cu or V/Cu. Stainless steel is exemplified as the microetched foil substrate.

At page 5, please replace the paragraph at lines 19-21 with the following:

U.S. patent Patent 6,478,853 (Hara et al.) reports a membrane for separation and dissociation of hydrogen which comprises an "amorphous" alloy comprising at least one of Zr, Hf and Ni. Exemplified membrane materials were described as as "ribbon-shaped" and "amorphous."

Please replace the paragraph bridging pages 5 and 6 with the following:

U.S. patent Patent 6,569,226 (Dorris et al.) reports membranes for hydrogen separation comprising a sintered homogeneous mixture of a ceramic composition and a metal where the metal may be Pd, Nb, Ta, V or Zr or a binary mixture of palladium with another metal such as Nb, Ag, Ta, V or Zr. Balachandran *et al.* reported mixed conducting ceramic and cermet membranes for hydrogen separation, although the exact compositions were not reported. (Balachandran, U.; Ma, B.; Maiya, P. S.; Mievile, R. L.; Dusek, J. T.; Picciolo, J.; Guan, J.; Dorris, S. E.; Liu, M. *Solid State Ionics* **1998**, *108*, 363; Balachandran, U.; Guan, J.; Dorris, S. E.; Bose, A. C.; Stiegel, G. J. In *Proceedings of the Fifth International Conference on Inorganic Membranes*: Nagoya, Japan, 1998; Balachandran, U.; Lee, T. H.; Dorris, S. E. In *Sixth International Pittsburgh Coal Conference*: Pittsburgh, PA, 1999.) Additionally, Balachandran *et al.* reported cermet membranes where the metal phase has high hydrogen permeability. (Balachandran, U.; Lee, T. H.; Zhang, G.; Dorris, S. E.; Rothenberger, K. S.; Howard, B. H.; Morreale, B.; Cugini, A. V.; Siriwardane, R. V.; Jr., J. A. P.; Fisher, E. P. In *26th International Technical Conference on Coal Utilization and Fuel Systems*: Clearwater, FL, 2001, pp 751-761; Balachandran, U.; Lee, T. H.; Wang, S.; Zhang, G.; Dorris, S. E.

In 27th International Technical Conference on Coal Utilization and Fuel Systems:  
Clearwater, FL, 2002, pp 1155-1165.)

At page 6, please replace the paragraph at lines 7-10 with the following:

U.S. ~~patents~~ Patents 4,857,080 (Baker et al.); 5,366,712 (Violante et al.); 5,518,530; 5,652,020 (Collins et al.); 5,674,302 (Sakai et al.); and 6,066,592 (Kawae et al.) relate to hydrogen separation membranes having a ceramic support coated with certain hydrogen permeable metals or certain palladium alloys.

At page 6, please replace the paragraph at lines 24-29 with the following:

Although a large volume of work has been conducted on proton-conducting ceramics (which herein are designated hydrogen ion-conducting ceramics), for example, metal oxides, oxyacid salts, and fluorides, relatively little work has related to mixed hydrogen ion/electron (or hole) conductors for hydrogen purification. U.S. ~~patents~~ Patents 5,821,185; 6,037,514 and 6,281,403 (White et al.) report perovskite-based ceramics which exhibit mixed hydrogen ion conduction and electron conduction having the general formula:

At page 7, please replace the paragraph at lines 3-6 with the following:

U.S. ~~patent~~ Patent 6,296,687 (Wachsman and Jiang) reported mixed hydrogen ion/electron conducting ceramics based on  $ACe_{1-x}M_xO_3$ , where A = Ba, Ca, Mb, Sr;  $[[B]]M = Eu$  or Tb, and  $0 < x < 1$ . Additionally, U.S. ~~patent~~ Patent 6,235,417 (Wachsman and Jiang) relates to a two-phase hydrogen separation membrane based on a perovskite and palladium.

At page 9, please replace the paragraph at lines 5-12 with the following:

In embodiments of the invention, the multi-layered membrane of the invention comprises one or more porous protective layers, a first catalyst layer, the NPSP layer, and a second catalyst layer and one or more porous protective layers, the layers listed ~~from~~ in order from the hydrogen feedstock surface of the membrane to the hydrogen sink surface of the membrane. In other related embodiments of the invention, the multi-

layered membrane of the invention comprises one or more porous protective layers, a first catalyst layer, the NPSP layer, a second catalyst layer and one or more porous protective layers, the layers listed from in order from the hydrogen feedstock surface of the membrane to the hydrogen sink surface of the membrane.

Please replace the paragraph bridging pages 9 and 10 with the following:

In specific embodiments, the hydrogen-permeable metal of the cermet is vanadium, niobium, tantalum, titanium, zirconium, or an alloy thereof, and particularly a binary, ternary or higher order alloy of vanadium, niobium, tantalum, titanium, or zirconium with one or more different metals selected from vanadium, niobium, tantalum, titanium, zirconium, aluminum, cobalt, chromium, iron, manganese, molybdenum, copper, nickel, gallium, germanium, tin, silicon, tungsten, lanthanum, beryllium and hafnium. Hydrogen-permeable metals of the cermets of the NPSP layer include, among others, vanadium, niobium, tantalum, zirconium or alloys thereof, alloys of vanadium, niobium, tantalum or zirconium with one or more of ~~titanium~~, nickel, titanium, aluminum, chromium, iron or copper. Hydrogen-permeable metals of the cermets of the NPSP layer include vanadium or alloys of vanadium with one or more of nickel, aluminum, titanium or mixtures thereof. Hydrogen-permeable metals of the cermets of the NPSP layer include alloys of vanadium with titanium and optionally one or more of nickel, or aluminum. In a specific embodiment, hydrogen-permeable metals include alloys of vanadium and titanium containing from about 1 to about 20 atom % titanium (and all subranges thereof). In another specific embodiment, hydrogen-permeable metals include alloys of vanadium and nickel containing from about 1 to about 20 atom % nickel (and all subranges thereof). Preferred ceramics useful in the cermets of the NPSP layer are chemically and mechanically stable under membrane operation conditions and unreactive with the metal of the cermet. Preferably for increased mechanical stability and longer useful membrane life, the ceramic and the metal of the cermet are selected to have similar thermal expansion characteristics. Ceramics of the cermet include metal oxides, e.g., alumina, zirconia, strontium titanate or mixtures thereof.

At page 11, please replace the paragraph at lines 1-7 with the following:

Where A is Ba or Sr, y is greater than zero, but less than 1;  $\delta$  is a number that renders the composition charge neutral and  $[[B]]$  B' is yttrium, cobalt, manganese or mixtures thereof. These hydrogen ion-conducting materials may be substantially single phase materials or materials exhibiting two or more distinguishable metal oxide phases. In specific embodiments, the hydrogen ion-conducting ceramic has stoichiometry of the above formula 2 where y is 0.8-0.9 and B' is cobalt or manganese.

At page 13, please replace the paragraph at lines 14-30 with the following:

Protective layers are porous metal oxide layers which if present are positioned as the outermost layers of the multi-layer hydrogen-permeable membranes. The protective layers protect the catalyst and NPSP layers from the detrimental effects of feedstream and other contaminants that may enter the membrane reactor system. For example, the protective layers can minimize undesired deposition of metals from the feedstream or from metal equipment, tubing or plumbing used in the membrane reactor system onto the catalyst or NPSP layer. Exemplary protective layers include alumina, zirconia, or other metal oxides. Additionally activated carbon or zeolites can be employed. Protective layers can also provide protection from chemical contaminants in the feedstock that would detrimentally affect membrane layer function. In particular, a metal oxide that forms stable sulfides can be used to protect the membrane from sulfur-containing compounds. For example, a ~~[[protectively]]~~ protective layer of porous ZnO, La<sub>2</sub>O<sub>3</sub>, SrO, CeO<sub>2</sub>, or perovskites such as SrCeO<sub>3</sub> or La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3- $\delta$</sub>  (where  $0 \leq x \leq 1$  and  $\delta$  is a number that renders the material charge neutral) can be used to protect the catalyst and NPSP layers from poisoning by sulfur-containing species, including hydrogen sulfide. Hydrogen sulfide dissociation is promoted by addition of copper to the metal oxide of the protective layer. In additional examples, a protectively layer comprising a ceramic or other material that absorbs or decomposes water or hydrocarbons can be provided.

At page 14, please replace the paragraph at lines 11-27 with the following:

In an alternative or additional embodiment, a hydrogen-permeable membrane of this invention is positioned in a membrane reactor which in addition comprises protective materials in a porous layer or bed separated from the membrane, but positioned with respect to the membrane such that hydrogen feed passes through the separate protective layer or bed prior to contacting the membrane. Similar separate protective layers or beds can also be provided to protect the hydrogen sink side of the membrane from contaminants that may be in or enter into the hydrogen sink. The membrane employed in such reactors may have no ~~protectively~~ protective layers or may have one or more protective layers as the outermost layers of the membrane. In specific embodiments, a reactor for separating hydrogen from a hydrogen-containing gas comprises in addition to a membrane of this invention one or more protective layers or beds containing alumina, zinc oxide or both separate from the membrane, but as positioned in the reactor, in fluid communication with the membrane such that feedstock passes through the protective layers or beds prior to contacting the membrane. A reactor may also comprise an additional protective layer or bed positioned to protect the hydrogen sink side of the membrane. The protective layer or bed can be provided for example as a porous bed of particulate metal oxide, containing, for example, alumina, zinc oxide or both, in close proximity or in contact with the membrane surface.

At page 16, please replace the paragraph at lines 9-12 with the following:

In other specific embodiments, the membranes and membrane reactors of this invention can be employed to carry out oxidation/reduction[[s]] reactions, including among others, hydrocarbon dehydrogenation reactions, aromatic coupling reactions, oxidative dimerization or oligomerization reactions, and hydrogen sulfide decomposition.

At page 18, please replace the paragraph at lines 5-10 with the following:

~~Fig. 17 is~~ Figure 17 shows H<sub>2</sub> permeation versus temperature for a 0.9-mm thick V/Ti alloy membrane (having 10 at. % Ti) at a differential pressure of 250 psi. A 0.5- $\mu$ m thick Pd film was deposited on each side of the membrane. The feed gas was 500

mL/min of 40H<sub>2</sub>/10He (bal N<sub>2</sub>) and [[a]] the sweep gas was 450 mL/min N<sub>2</sub>. The maximum permeability was  $1 \times 10^{-7} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$ . This data shows that an operational temperature of less than 100°C under H<sub>2</sub> can be used without membrane failure when Ti is added to V.

At page 18, please replace the paragraph at lines 11-13 with the following:

Figure 18[.]shows H<sub>2</sub> permeation as a function of the H<sub>2</sub> partial pressure difference across a V-Ti alloy membrane. This data indicates that increasing the feed and sweep flows facilitates H<sub>2</sub> transport.

At page 18, please replace the paragraph at line 24 with the following:

~~Fig.~~ Figure 24 is a schematic drawing of an exemplary reactor of this invention in cross-section.

At page 20, please replace the paragraph at lines 17-26 with the following:

Metal oxide layers may be formed by oxidation processes at the interface of two materials where one or both of the materials contain one or more metals. Such metal oxide layers may form spontaneously during membrane fabrication or operation of the membrane on contact with oxidizing gases. Such layers may provide some of the benefits of the barrier layers herein. However, since the formation of such metal oxide layers may not be consistent in composition or thickness, it is preferable to provide a barrier layer of selected thickness and composition, by design when needed or desirable. A barrier layer comprising a metal oxide layer comprising one or more metals of the catalyst or NPSP layer can be formed by controlled oxidation of the surface of the catalyst or NPSP layer. These layers are sufficiently porous or hydrogen permeable, such that they do not ~~to~~ impede hydrogen permeation.

At page 21, please replace the paragraph at lines 1-11 with the following:

In a specific embodiment, layers 1 and [[8]] 9 are porous ceramic layers for protecting the inner layers of the membrane from detrimental feedstream contaminants, which may originate in the feedstream source, from materials in the reactor or the



reactor system, including any tubing or plumbing for carrying the feedstream or removing hydrogen-enriched gas. For example, the porous protective layer can trap Fe, Cr or other metals originating from stainless steel component of the reactor system. Metal oxides suitable for use as protective layers include, among others, alumina, titania, or zirconia. In a preferred embodiment, alumina is employed as a protective layer. In addition, activated carbon and zeolites may also be used in protective layers. In a specific embodiment, layers 1 and [[8]] 9 have porosity between about 30-60% with macropores (i.e., pores > 200 nm in diameter). In another specific embodiment, layers 1 and [[8]] 9 are porous and high surface area ceramic layers.

At page 21, please replace the paragraph at lines 24-28 with the following:

In a specific embodiment, layers 2 and 8, if one or both are present, are porous layers of zinc oxide, which ~~functions~~ function for removal of hydrogen sulfide. Membranes of this invention can have one, two, or more chemically or physically distinguishable porous protective layers on either side, preferably on the feedstream side of the membrane. Layers 2 and 8, if both present may be chemically and physically the same, or chemically and physically different.

At page 23, please replace the paragraph at lines 5-31 with the following:

Hydrogen-Permeable Metals and Alloys. High hydrogen permeability of transition metals has been well documented over many decades. In particular, Group V metals (V, Nb, Ta) and related alloys have exceptional permeability (See: U.S. ~~patent~~ Patent 3,350,846, among others). There are a number of reports of metal and alloy materials, particularly metal foils, used for hydrogen separation and purification. (See: Makrides, A. C.; Wright, M. A.; Jewett, D. N., "Separation of Hydrogen by Permeation," 3,350,846, November 7, 196; Hill, E. F., "Hydrogen Separation Using Coated Titanium Alloys," 4,468,235, August 28, 1984; Hara, S.; Sakaki, K.; Itoh, N., "Amorphous Ni Alloy Membrane for Separation/Dissociation of Hydrogen, Preparing Method and Activating Method Thereof," 6,478,853, November 12, 2002; Edlund, D. J.; Pledger, W. A.; Studebaker, T., "Hydrogen-Permeable Metal Membrane and Hydrogen Purification Assemblies Containing the Same," 6,547,858, April 15, 2003; Buxbaum, R. E.,

"Composite Metal Membrane for Hydrogen Extraction," 5,215,729, June 1, 1993; Edlund, D. J., "Hydrogen-Permeable Composite Metal Membrane," 5,139,541, August 18, 1992; Edlund, D. J.; Friesen, D. T., "Hydrogen-Permeable Composite Metal Membrane and Uses Thereof," 5,217,506, June 8, 1993; Edlund, D. J., "Composite Hydrogen Separation Metal Membrane," 5,393,325, February 28, 1995; Edlund, D. J.; Newbold, D. D.; Frost, C. B., "Composite Hydrogen Separation Element and Module," 5,645,626, July 8, 1997; Thornton, P. H., "Supported Membrane for Hydrogen Separation," 6,475,268, November 5, 2002; Peachey, N. M.; Dye, R. C.; Snow, R. C.; Birdsell, S. A., "Composite Metal Membrane," 5,738,708, April 14, 1998; Dye, R. C.; Snow, R. C., "Thermally Tolerant Multilayer Metal Membrane," 6,214,090, April 10, 2000; Buxbaum, R. E.; Marker, T. L. *J. Mem. Sci.* **1993**, *85*, 29-38; Peachey, N. M.; Snow, R. C.; Dye, R. C. *J. Mem. Sci.* **1996**, *111*, 123-133; Nishimura, C.; Komaki, M.; Amano, M. *Mat. Trans.* **1991**, *32*, 501-507; Yamakawa, K.; Ege, M.; Ludescher, B.; Hirscher, M.; Kronmueller, H. *J. Alloys and Compounds* **2001**, *321*, 17-23; Zhang, Y.; Ozaki, T.; Komaki, M.; Nishimura, C. *Scripta Materialia* **2002**, *47*, 601-606; Heinze, S.; Vuillemin, B.; Colson, J.-C.; Giroux, P.; Leterq, D. *Solid State Ionics* **1999**, *122*, 51-57; Nishimura, C.; Komaki, M.; Hwang, S.; Amano, M. *J. Alloys and Compounds* **2002**, *330-332*, 902-906.)

Please replace the paragraph bridging pages 26 and 27 with the following:

The ranges listed in Table 1 show the maximum amount of each metal that can be added to a selected amount of vanadium and still maintain the bcc structure. To use the information in Table 1, a content of V is first selected. For example, [[a]] an alloy of 80 at % V will have 20 at. % total of a second metal or 20 at. % of a combination of a second and a third metal. To prepare a binary or ternary vanadium-aluminum-copper alloy containing 80 at. % V and which retains bcc structure, up to about 5 at. % Cu and/or up to about 20 at. % Al is combined with the V. Examples of ternary bcc alloys of vanadium include, an alloy containing 80 at. % V, 19.9 at. % Al and 0.1 at.% Cu , an alloy containing 80 at. % V, 15 at. % Al and 5 at. % Cu. A V-Al-Cu alloy having bcc structure can not have more than 40 at. % Al or more than 5 at. % Cu. A V-Al-Mo alloy which retains a bcc structure can not have more than 40 at. % Al, but the amount of Mo

present will not effect the bcc structure. Known phase diagrams can be employed, as is understood by those of ordinary skill in the art, to determine the at. % ranges of second and third metals that can be added to any of niobium, tantalum, or zirconium to prepare binary and ternary alloys which retain bcc structure. Useful phase diagrams are available for example, in Handbook of Ternary Alloy Phase Diagrams, (P. Villars, A. Prince, H. Okamoto; Materials Park, OH: ASM International, 1995) and Binary Alloy Phase Diagrams, Ed. T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak; Materials Park, OH: ASM International, 1990).

Please replace the paragraph bridging pages 27 and 28 with the following:

The hydrogen permeable cermet of the NPSP layer can be a cermet where hydrogen permeation occurs primarily through the metal phase and the function of the ceramic phase is primarily structural. The ceramic may or may not be permeable to hydrogen. The metal phase content is between about 30 and 99 vol. %, and preferably between 60 and 80 vol. %. Useful hydrogen-permeable metals include Group IVB or VB metals and alloys thereof, including alloys of the Group IVB or VB metals with each other or with any transition metal. Various suitable hydrogen-permeable metals and alloys are known to the art (for example, see U.S. ~~patents~~ Patents 5,215,729; 5,139,541; 5,217,506; 5,393,325, 6,214,090, and Buxbaum, R. E.; Marker, T. L. *J. Mem. Sci.* **1993**, *85*, 29-38.) In preferred embodiments the hydrogen-permeable metal of the cermet is not palladium or an alloy containing palladium. In specific embodiments, hydrogen-permeable metals of the cermets of the NPSP layer include, among others, vanadium, niobium, tantalum or alloys thereof, and alloys of vanadium, niobium, zirconium or tantalum with one or more of nickel, cobalt, iron, titanium, chromium, aluminum, or copper. In other specific embodiments, hydrogen-permeable metals of the cermets of the NPSP layer include vanadium or alloys of vanadium with one or more of titanium, nickel, aluminum, ~~titanium~~ or chromium.

At page 28, please replace the paragraph at lines 7-15 with the following:

The hydrogen permeable cermet of the NPSP layer can alternatively be a cermet where hydrogen permeation occurs substantially or primarily through the ceramic

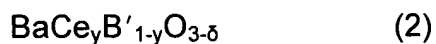
phase. The metal phase may or may not be hydrogen permeable. The ceramic and metal may ~~additional~~ additionally provide structural stability. The ceramic may be a hydrogen ion-conducting ceramic which does not necessarily exhibit substantial electron conduction or the hydrogen ion-conducting ceramic may be a mixed conducting ceramic which additionally exhibits substantial electron conduction. The hydrogen ion-conducting ceramic may be a single phase ceramic or a multiple phase ceramic. The metal phase content is between about 30 and 99 vol.%, preferably between about 20 and 60 vol. %), and more preferably between about 30 and about 50 vol.%.

Please replace the paragraph bridging pages 28 and 29 with the following:

Metal and Metal Alloy Catalysts. Because many of the metals and alloys with the highest hydrogen permeability (metals and alloys other than those containing Pd) are easily poisoned and lack sufficient catalytic activity for hydrogen dissociation, a thin layer of a protective catalytic metal, such as Pd, is applied to the membrane surface to enable sustained hydrogen permeation. In this way the bulk of the membrane can be a relatively inexpensive material with very high permeability and the expensive catalytic Pd layer can be provided as a very thin film. Many metal and alloy catalyst layers are known to the art and suitable for several embodiments of this invention. Examples include metals and alloys from Group IB, VIIB, and VIIIB (for example, see U.S. patent Patent 5,139,541.)

Please replace the paragraph bridging pages 35 and 36 with the following:

Hydrogen ion-conducting ceramics further include those having the stoichiometry:



where y is greater than zero, but less than 1;  $\delta$  is a number that renders the composition charge neutral and  $\text{B}'$  is yttrium, cobalt, manganese or mixtures thereof. In specific embodiments, the hydrogen ion-conducting ceramic has stoichiometry of the above formula 2 where y is 0.8-0.9 and B' is cobalt or manganese. Materials prepared to have

the stoichiometry of formula 2 may contain metal oxide phases in addition to a hydrogen ion-conducting perovskite phase. Hydrogen ion-conducting phases may or may not additionally conduct electrons. The additional phases may or may not conduct hydrogen ion and/or electrons.

Please replace the paragraph bridging pages 39 and 40 with the following:

~~Figure~~ Figures 1B through 1E schematically illustrate four exemplary embodiments of the invention. Figure 1B illustrates a multilayer membrane in which a hydrogen permeable central layer is separated from metal or metal alloy catalysts by use of layers of barrier coatings. The primary function of the central metal or alloy layer is to selectively permeate (purify) hydrogen. The primary function of the barrier coating is to minimize interdiffusion of metals between the central and catalyst layers. The primary function of the catalyst is to split hydrogen into atoms or ions suitable for permeation through the barrier and central layers. The barrier coating and catalyst layers on either side of the membrane may be made of the same or different materials.

At page 41, please replace the paragraph at lines 23-27 with the following:

This invention provides membrane reactors which employ membranes of this invention for hydrogen separation. Various reactor membrane designs are known and used in the art. A number of references cited herein provide useful reactor designs. U.S. ~~patents~~ Patent 6,281,403, 6,037,514, and 5,821,185 provide descriptions of exemplary reactors. U.S. ~~patent~~ Patent 6,569,226 also provides a description of an exemplary reactor.

At page 42, please replace the paragraph at lines 13-20 with the following:

The invention also relates to methods for separating hydrogen from other components in a hydrogen-containing gas. Exemplary feedstreams from which hydrogen can be separated include water-gas shift mixtures and mixtures resulting from petroleum reforming. The membranes and reactors of this invention can be used to separate hydrogen from gas mixtures containing hydrocarbons (e.g., methane, ethane, butane, etc.), aromatic species (e.g., benzene, naphthalene, etc.), nitrogen containing

species (e.g., ammonia, etc.), oxidized hydrocarbons (e.g., ethanol and/or other alcohols)[[.]]and sulfur containing species (e.g., hydrogen sulfide, sulfur dioxide, etc.)

At page 43, please replace the paragraph at lines 3-8 with the following:

Exemplary feedstreams from which hydrogen can be separated include water-gas shift mixtures and mixtures resulting from petroleum reforming. The membranes and reactors of this invention can be used to separate hydrogen from gas mixtures containing hydrocarbons (e.g., methane, ethane, butane, etc.), aromatic species (e.g., benzene, naphthalene, etc.), nitrogen containing species (e.g., ammonia, etc.), oxidized hydrocarbons (e.g., ethanol and/or other alcohols)[[.]]and sulfur containing species (e.g., hydrogen sulfide, sulfur dioxide, etc.)

At page 43, please replace the paragraph at lines 9-13 with the following:

The invention further relates to methods for carrying out various chemical reactions, particularly oxidation-reduction reactions. In these reactions, hydrogen is removed from at least one [[a]] hydrogen-containing species (hydrocarbon, hydrogen sulfide, etc.) on the hydrogen source side of the membrane and transported to the other side of the membrane to reduce an oxidized species (e.g., oxygen) or to be released as hydrogen to facilitate the reaction.

At page 44, please replace the paragraph at lines 9-15 with the following:

In application to oxidative dimerization or oligomerization reaction, a hydrocarbon oligomerization catalyst is provided on the surface of the membrane in contact with the hydrogen-containing species and a reduction catalyst is provided on the hydrogen sink surface of the membrane. For example, a) oxides of the first row transition metals supported on the alkali metal oxides, b)[[.]] the metals Ni, Fe, Pt, Ag or Pd and their alloys, and/or c) perovskite compounds  $AB_{1-x}B'_xO_{3-y}$ , where A = Ca, Sr, Ba, B= Ce, Tb, Pr, or Th; B' = Ti, V, Cr, Mn, Fe, Co, Ni or Cu and  $0.02 < x < 0.5$  and y is a number that renders the compound charge neutral).

At page 46, please replace the paragraph at lines 1-9 with the following:

1. A 60 vol. % V/alumina cermet is prepared by combining 4.19 g vanadium metal (-325 mesh, 99.5% metals basis, Alfa Aesar) with 3.81 g aluminum oxide (alpha-alumina, 0.35-0.49  $\mu\text{M}$ , 99.95% Alfa Aesar). A sintering aid (0.04 g  $\text{Y}_2\text{O}_3$ ) and organic binder (0.16 g, polyvinyl butryal, ~~DVB~~ PVB) can also be added. The mixture is thoroughly mixed under conditions that prevent oxidation of the vanadium. The mixture is mixed dry, or under inert atmosphere, or using either a minimum amount of solvent, or an oxygen-free solvent. The combination is pressed in a 1/2 inch diameter die uniaxially at 17,000 lbs for at least about 2 minutes at 130°C. The pressed disks are then heated to 1650°C under vacuum ( $10^{-4}$  to  $10^{-5}$  torr) for 2 to 4 hrs until dense. Figure 2 provides an XRD spectrum of the ground disk surface of the cermet formed.

At page 46, please replace the paragraph at lines 19-23 with the following:

3. Vanadium-zirconia cermets are prepared by combining powders of ~~vanadium~~ vanadium metal, yttria-stabilized zirconium oxide (Tosoh-Zirconia, TZ-8Y) and organic binder PVB. The combined materials are mixed as in 2. The combinations are pressed into a desired shape (disks of approximate selected thickness), sintered at 1600°C in vacuum and ground to a selected thickness. Figure 3 is an XRD spectrum of the ground surface of the disk.

At page 56, please replace the paragraph at lines 1-9 with the following:

As evident in the figure, this material demonstrates good long-term stability, which suggests resistance to hydrogen embrittlement under operating conditions. Analogous membranes without a protective coating have significantly ~~shorted~~ shortened operational lifetimes and are more susceptible to failure. For this category of membranes, hydrogen embrittlement can be avoided by maintaining the membrane above approximately 300°C. Prior to cooling the membrane, the separation cell first is purged with an inert gas for several hours. Once an inert atmosphere is established and residual hydrogen is liberated from the membrane, the sample can be cooled to room temperature and subsequent sample analysis indicates no metal hydride is present.

At page 58, please replace the paragraph at lines 6-11 with the following:

Figure 17 shows H<sub>2</sub> permeation versus temperature for a 0.9-mm thick V/Ti alloy membrane (having 10 at. % Ti) at a differential pressure of 250 psi. A 0.5-μm thick Pd film was deposited on each side of the membrane. The feed gas was 500 mL/min of 40H<sub>2</sub>/10He (bal N<sub>2</sub>) and the sweep gas was 450 mL/min N<sub>2</sub>. The maximum permeability was  $1 \times 10^{-7} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$ . This data shows that an operational temperature of less than 100°C under H<sub>2</sub> can be used without membrane failure when Ti is added to V.

At page 58, please replace the paragraph at lines 12-17 with the following:

Figure 18 shows H<sub>2</sub> permeation as a function of the H<sub>2</sub> partial pressure difference across a 0.5-mm thick V-Ti alloy (10 at. % Ti) with 0.3 μm of Pd on each side of the membrane. The H<sub>2</sub> feed and sweep partial pressures are  $p_f$  and  $p_s$ , respectively. The feed gas was 1.5 L/min of 80 vol.% H<sub>2</sub>/10 vol.% He/10 vol.% N<sub>2</sub>. The sweep gas was 1.1 L/min N<sub>2</sub>. The maximum permeability was  $2.7 \times 10^{-7} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$ . The temperature was 400°C. This data indicates that increasing the feed and sweep flows facilitates H<sub>2</sub> transport.

At page 58, please replace the paragraph at lines 18-25 with the following:

Figure 19 shows H<sub>2</sub> permeability as a function of the H<sub>2</sub> partial pressure difference across a 0.6-mm thick V-Ti alloy membrane (15 at.% Ti) with 0.3 μm of Pd on each side. The membrane temperature was 438°C. The feed gas was 80 vol.% H<sub>2</sub>/3 vol.% He (bal. Ar) at 1.5 L/min. The maximum permeability was  $3.6 \times 10^{-7} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$ . The sweep gas was 1.5 L/min Ar. The line corresponds to the expected trend for Sieverts' Law. This data shows that similar results are obtained with both the V-10Ti and V-15Ti alloys. Also, deviation from Sieverts' law occurs at high partial pressure differentials likely due to inadequate H<sub>2</sub> supply rate on the feed side.



At page 59, please replace the paragraph at lines 11-17 with the following:

Figure 23 shows H<sub>2</sub> permeation as a function of the H<sub>2</sub> partial pressure difference across the membrane. The H<sub>2</sub> feed and sweep partial pressures are  $p_f$  and  $p_s$ , respectively. The membrane was a 0.7-mm thick V-Ti alloy (10 at. % of Ti) with 0.3  $\mu\text{m}$  of Pd on each side. The feed gas was varied from 8.3 L/min of 60 vol.% H<sub>2</sub>/40 vol.% He and 5.3 L/min pure H<sub>2</sub>. The sweep gas was 5 L/min Ar. The maximum permeability was  $2.6 \times 10^{-7} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$ . The temperature was 442°C. (This data can be compared to Figures above and further indicates that increasing the feed and sweep flows facilitates H<sub>2</sub> ~~transport~~. transport).

At page 65, please replace the paragraph at lines 3-9 with the following:

This invention provides hydrogen-permeable membranes for separation of hydrogen from hydrogen-containing gases. The membranes are multi-layer having a central hydrogen-permeable layer with one or more catalyst layers, barrier layers, and/or protective layers. The invention also relates to membrane reactors employing the hydrogen-permeable membranes of the invention and to methods for separation of hydrogen from a hydrogen-containing gas using the membranes and reactors. The reactors of this invention can be combined with additional reactor systems for direct use of the separated hydrogen.